

The following problems must be solved without approximations. The purpose is to learn how to use the mass balance, and charge balance equations combined with appropriate equilibrium expressions to calculate the concentration of all the species. Solve all problems in complete equation form. Then, find the numerical answers. It is up to you to select appropriate numerical calculation tools (calculator, computer, internet sites etc.) to reach the final answer. Use tables to obtain  $K_a$ ,  $K_b$  and  $K_w$ .

**1. (Weak and very dilute base in aqueous solution)**

A very dilute weak base is made in an aqueous solution. Consider  $10^{-10}$  M  $\text{NH}_3$  in water. Derive and calculate the concentrations of all the species present in such a dilute solution. Proceed as follows:

- Identify all the species:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{NH}_4^+$ ,  $\text{NH}_3$ . These are four free species in equilibrium. Therefore, we need 4 equations
- Mass balance: Total  $\text{NH}_3$ ,  $10^{-10} = \text{NH}_4^+ + \text{NH}_3$  (eq. 1)
- Charge balance:  $\text{H}^+ + \text{NH}_4^+ = \text{OH}^-$  (eq. 2)
- $K_b$  for  $\text{NH}_3$ :  $K_b = (\text{NH}_4^+ \times \text{OH}^-) / \text{NH}_3$  (eq. 3)
- $K_w = \text{H}^+ \cdot \text{OH}^-$  (eq. 4)

**2. (Salt of a diprotic acid)**

(a) Consider a solution of 0.001 M  $\text{NaHSO}_3$  as the salt of the diprotic acid,  $\text{H}_2\text{SO}_3$  (sulfurous acid:  $\text{p}K_{a1} = 1.91$ ,  $\text{p}K_{a2} = 7.18$ ). Calculate the pH and the concentrations of all the species in solution without approximations. (Hint: First, identify the number and type of species, write the same number of equations, derive the species equations without approximations, and then find and concentrations of all the species).

(b) By using the equations derived in problem 2(a), calculate the concentrations of  $\text{H}_2\text{SO}_3$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$  at pH 2, 4, 6, 8, 10, and 12. Plot the data and explain your findings.